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模拟混凝土孔隙液中钢筋腐蚀行为及其混  
凝土碳化作用的研究

Study on the Carbonation of Concrete and the Corrosion  
Behavior of Reinforcing Steel in Simulated Concrete Pore  
Solutions

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**Study on the Carbonation of Concrete and the Corrosion Behavior of  
Reinforcing Steel in Simulated Concrete Pore Solutions**



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Fulfillment of the Requirement for the Degree of  
**Master of Science**

By

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## 摘要

钢筋腐蚀导致钢筋混凝土结构耐久性降低,造成钢筋混凝土结构过早失效的现象在当今世界十分普遍,给世界各国的生产和生活带来巨大的损失。因此,研究钢筋的腐蚀机理具有重要的现实意义。混凝土中钢筋是否发生腐蚀取决于维持其表面钝化膜稳定性的环境条件,氯离子侵蚀和混凝土碳化是导致钢筋表面去钝化发生腐蚀的主要原因。本工作采用电化学技术,结合现代表面分析方法,研究 R235 钢筋在不同 pH 值模拟混凝土孔隙液中的腐蚀行为,考察 304 不锈钢钢筋表面钝化膜半导体特性与其耐蚀性之间的关联,同时模拟混凝土碳化过程,研究混凝土中钢筋的腐蚀电化学行为。主要研究内容和结果如下:

(1) 应用电化学阻抗谱和极化曲线测试方法,结合扫描电子显微镜技术,研究 R235 钢筋在模拟混凝土孔隙液中的腐蚀行为,初步探明了介质 pH 值对 R235 钢筋腐蚀的影响机制。结果表明,钢筋在高碱性模拟液中表面保持钝化状态,随着模拟液 pH 值的降低,钢筋的腐蚀速度升高,钝化膜稳定性下降,引起钢筋表面去钝化发生局部腐蚀的临界 pH 值在 11.12~11.05 之间。

(2) 初步探明了 304 不锈钢钢筋表面钝化膜在不同 pH 值和氯离子浓度的模拟混凝土孔隙液中的半导体性质与其耐蚀性之间的关联。结果表明,钢筋表面钝化膜呈现出 n 型半导体性质,随着模拟液 pH 值降低,浅层施主浓度增加,深层施主浓度减小。在含氯离子溶液中浸泡 1 h 后 (pH 12.50),钝化膜的 n 型半导体结构没有发生变化,浅层施主浓度和深层施主浓度均随着氯离子浓度的增加而增大,钝化膜稳定性下降,钢筋耐蚀性降低。

(3) 利用碳酸盐高温热氧化法制备 W/WO<sub>3</sub> pH 电极,结合 XRD、Raman、SEM、EDS、XPS 等分析技术对 WO<sub>3</sub> 膜层进行表征,考察了膜层的组成与表面形态及其对 pH 响应行为的影响。结果表明,研制的 W/WO<sub>3</sub> 电极具有良好的稳定性、灵敏度以及测试准确度,在较宽的 pH (2~13) 范围内线性响应好,适用于检测混凝土中的 pH 值。将所研制的 W/WO<sub>3</sub> 电极作为 pH 探针,原位检测模拟混凝土碳化过程中的 pH 值变化,结合电化学技术(半电池电位法、电化学阻抗谱)研究混凝土中 R235 钢筋的腐蚀电化学行为。结果表明,随着碳化时间的延

长，电荷转移电阻  $R_{ct}$  总体呈现出减小的变化趋势，钢筋钝化膜稳定性下降，钢筋耐蚀性降低，发生腐蚀的倾向加剧。

**关键词：**R235 钢筋；304 不锈钢；钝化膜；电化学技术；pH 电极

厦门大学博士论文摘要库

## Abstract

The decline in the durability and the premature failure of reinforced concrete structures due to the reinforcing steel corrosion has become a widespread phenomenon and caused a huge loss in countries all over the world. Thus, further study of the corrosion mechanism of reinforcing steel is of great practical significance. Whether or not the reinforcing steel in concrete maintains its passivity depends on the conditions of steel/concrete interface. Generally speaking, the two main reasons which results in the depassivation of reinforcing steel in concrete are carbonation of concrete and penetration of chloride ions. In the present work, electrochemical measurements, combined with surface analysis techniques were used to study the corrosion behaviour of reinforcing steel (R235) in simulated concrete pore solutions (SPS) with different pH values, explore the correlation between semiconductor properties and corrosion resistance for the passive film of 304 stainless steel, and research the corrosion behaviour of reinforcing steel (R235) in carbonated concrete specimens. The main progress and results of this work are as follows:

(1) Linear polarization, potentiodynamic anodic polarization, electrochemical impedance spectroscopy combined with scanning electron microscopy were used to study the mechanism of the steel (R235) corrosion induced by the decrease of pH value of SPS. The results indicated that the steel remained passive state in the highly alkaline SPS, with the decrease of the pH value, the steel corrosion rate increased, the passive film stability decreased, and the critical pH value for localized corrosion of reinforcing steel in SPS solutions was between 11.12 and 11.05.

(2) Correlation of semiconductor properties and corrosion resistance for the passive film formed on 304 stainless steel with different pH values and chloride ion concentrations in SPS was observed. The results showed that the passive film on the stainless steel surface behaved as n-type semiconductor, the shallow donor concentration increased while the deep donor concentration decreased with the pH

value decreasing. Immersed in the SPS (pH 12.50) with  $\text{Cl}^-$  for 1 h, the passive film still behaved as n-type semiconductor. With the increase of chloride ion concentration, both the shallow donor concentration and the deep donor concentration increased, the passive film stability decreased, which reduced the corrosion resistance of steel.

(3) The  $\text{W}/\text{WO}_3$  pH electrode was prepared by thermal oxidation in carbonate. The response of the electrode to pH values depended on the composition and surface morphology of  $\text{WO}_3$  film which was analyzed by XRD, Raman, SEM, EDS and XPS. The results demonstrated that the prepared  $\text{W}/\text{WO}_3$  electrode had good stability, sensitivity, accuracy and potential response in a wide pH values (2~13) range. The electrode was useful for in situ and long term monitoring of the pH values in concrete. The electrochemical methods (half-cell potential measurement and the electrochemical impedance spectroscopy), were applied to study the corrosion behaviour of reinforcing steel (R235) in concrete. The prepared  $\text{W}/\text{WO}_3$  probes were embedded in concrete for in situ monitoring of the pH variation during concrete carbonation. The results revealed that, with the carbonation time increasing, both the charge transfer resistance  $R_{ct}$  and the passive film stability decreased, the corrosion resistance of steel reduced, and the steel was prone to corrosion.

**Key Words:** R235 Reinforcing Steel; 304 Stainless Steel; Passive Film; Electrochemical Techniques; pH Electrode.

## 第一章 绪 论

### 1.1 钢筋混凝土结构

混凝土是由胶凝材料（水泥）、粗和细骨料（石料和砂料）、水和外加剂按一定的配合比，经均匀搅拌、密实成型并硬化而形成的一种人造石材<sup>[1]</sup>。以混凝土材料为主，并根据需要配置钢筋、预应力钢筋、钢骨、钢管、纤维等，共同受力的结构均可称为混凝土结构<sup>[2]</sup>。自从 19 世纪 20 年代波特兰水泥问世以来，混凝土结构因具有来源广泛、成本低廉、坚固耐用等优点，作为主要的建筑材料，大量应用于各种工程，成为使用最为广泛的人造建筑材料<sup>[3]</sup>。工程中最常用的是由钢筋和混凝土两种材料组成共同受力的钢筋混凝土结构。这种结构的发展变化可以简要概述如下<sup>[2]</sup>：最早出现的是采用低强度的混凝土和钢筋组合构成的钢筋混凝土板、梁、柱等简单构件；随着两种材料强度性能的提高，开始出现预应力混凝土结构和大跨度结构；至今，依托采用装配式钢筋混凝土结构、泵送商品混凝土等工业化生产方式，许多超高层建筑、特长隧道、特长跨海大桥等大型结构不断涌现出来。

钢筋的抗压抗拉能力都很强。混凝土抗压能力强，但是抗拉能力较弱，混凝土承受拉力时很容易发生开裂，需要通过添加配筋提高其承载力。钢筋与混凝土之间存在有粘结力，二者可以相互作用共同受力；两种材料的温度线膨胀系数也很接近（混凝土为  $1.0 \sim 1.4 \times 10^{-5} \text{ K}^{-1}$ ，钢筋为  $1.2 \times 10^{-5} \text{ K}^{-1}$ ）<sup>[2]</sup>。将混凝土和钢筋两种材料结合在一起共同工作，利用混凝土抗压、钢筋抗拉，则能使两种材料发挥各自所长，组成性能优良的结构构件以满足不同工程受力的要求并取得良好的经济社会效益，这就是钢筋混凝土结构得到广泛应用的主要原因。

### 1.2 钢筋混凝土结构的耐久性及其腐蚀破坏的危害性

长久以来，因受混凝土是一种耐久性能优良的建筑材料传统观念影响，人们较少关注钢筋混凝土结构的腐蚀破坏问题。混凝土结构耐久性是指混凝土结构及其构件在可预见的工作环境及材料内部因素的作用下，在预期的使用年限内抵



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